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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08L 23/04, C08J 5/18	A1	(11) International Publication Number: WO 94/06857 (43) International Publication Date: 31 March 1994 (31.03.94)
(21) International Application Number: PCT/US93/08586 (22) International Filing Date: 13 September 1993 (13.09.93) (30) Priority data: 07/945,769 16 September 1992 (16.09.92) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: HODGSON, William, John, Jr. ; 1601 South- wood, Baytown, TX 77520 (US). HALLE, Richard, Wayne ; 11810 Orchard Mountain Drive, Houston, TX 77059 (US). PIERCE, Charles, Lillard ; 7423 Willow Oak, Baytown, TX 77521 (US).		(74) Agents: SHER, Jaimes et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US). (81) Designated States: BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SOFT FILMS HAVING ENHANCED PHYSICAL PROPERTIES (57) Abstract The present invention provides for a polymer composition comprising a blend of from 25 to 90 % by weight of a very low density ethylene polymer having a density on the range of from 0.88 to 0.925 g/cm ³ , a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution not greater than 3.5 and a compositional distribution breadth index greater than 70 %, and from 10 to 75 % by weight of a low to medium density ethylene polymer having a density of from 0.910 to 0.935, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution greater than 3.5 and a compositional breadth index less than 70 %. The invention also provides for films prepared from this blend having single layer construction or having laminar ABA construction wherein the A or skin layers comprise the blend of this invention and the B or core layer comprises a different olefin polymer such as high density polyethylene. Films of this invention exhibit excellent elongation, tensile and impact properties and also softness, feel and noise properties which render them eminently suitable for use as back sheet components in the fabrication of absorbent articles such as diapers, bed pads and like articles where such properties are desirable.		

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disclosed in U.S. Patents 4,076,698 and 4,205,021.

Despite the good properties of films made using LLDPE, the melt processing properties of the polymer tend to restrict the process conditions under which cast films having a uniform thickness can be made. For example, a typical process for preparing an embossed film for use as diaper backsheet material is the slot-die cast extrusion process wherein the polymer is heated to a temperature generally in the profile range of about 175°C to about 290°C (350°F to 550°F) in an extruder and extruded through a slot die into the nip of a steel and rubber roll system. Where the film is to be embossed, the steel roll is engraved with a pattern of either protrusions (a male embossing roll) or depressions (a female embossing roll). The rubber roll serves as a backing roll into which the steel roll pattern is impressed during the formation of the film. Thus the roll system serves both to film-form and texture the polyolefin material. The speed of the rubber and steel rolls is maintained to permit continuous embossing of the film and subsequent take up of the film on a wind up roller after it exits the steel/rubber roller nip.

In terms of process efficiency, the film manufacturer is highly motivated to adjust processing conditions such as temperature, roll speeds and take-up speeds to maximize the rate of film production on the one hand while on the other hand producing a quality film having a substantially uniform film thickness, which is generally in the range of about 19 μ to about 51 μ (0.75 to 2 mils).

A particular property of LLDPE which tends to restrict the line speed at which film made from this polymer can be processed is caused by a phenomena referred to as draw resonance. Draw resonance is defined as the inability of the film to hold a constant film thickness down the film web in the machine or take-up direction, which is evidenced by the presence of light and dark bands running across the film. The light areas are a thinner gauge and the darker areas are of a thicker gauge. The degree of draw resonance is a direct function of line speed, becoming worse at higher line speeds. As a result, the maximum line speed at which good quality film can be produced is restricted by the onset of draw resonance.

Attempts have been made to improve the draw resonance of LLDPE by utilizing a blend of this material with up to 50% by weight of another polyethylene having a higher Melt Index than LLDPE, such as high pressure low density polyethylene (LDPE) having a Melt Index of at least 7.5 dg/min and a density in the range of from 0.910 to 0.930 g/cm³ or as an alternative EVA's can be blended with LLDPE. However, draw resonance is still found to occur at higher line speeds

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(e.g., 254 cm/sec (500 ft/min)) with such blends and the presence of a substantial amount of the LDPE in the blend serves to diminish the good tensile and elongation properties of film material when compared with material containing LLDPE as the sole polymer.

5 Recently, a new class of low density ethylene polymers have been introduced into the marketplace. These materials are characterized as very low density ethylene polymers having a density in the range of from 0.88 to 0.915 g/cm³, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution (MWD) of no greater than 3.5 and a compositional distribution breadth index (CDBI) greater than 70 percent. Compositionally, these polymers contain ethylene
10 copolymerized with up to 15 mole % of another alpha monoolefin containing from 3 to 20 carbon atoms such as butene-1, hexene-1, octene-1 and the like. These polymers with narrow MWD and narrow CD provide a unique balance of properties including narrow melting point range and improved toughness when
15 fabricated into shaped articles as compared with normal low density polyethylene prepared by the conventional Ziegler catalyst systems.

 One of the primary uses of such materials is as a heat seal component as is shown in PCT Publication No. WO/93/03093 or layer used in conjunction with the preparation of packaging films constructed from polyolefin polymers such as
20 polypropylene as is shown in PCT Publication No. WO/92/14784. The narrow melting point range of these polymers renders them extremely useful in packing fill operations where it is desirable to develop strong seal strength immediately after packaging and while the film is still hot from the sealing operation.

SUMMARY OF THE INVENTION

25 The present invention provides for a polymer composition comprising a blend of from 25 to 90% by weight of a very low density ethylene polymer having a density on the range of from 0.88 to 0.925 g/cm³, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution not greater than 3.5 and a compositional distribution breadth index greater than 70%, and from 10 to 75%
30 by weight of a low to medium density ethylene polymer having a density of from .910 to .935 g./cm³, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution greater than 3.5 and a compositional breadth index less than 70%.

 The polymer composition of this invention may be fabricated into film material by cast extrusion processes and exhibit improved draw resonance such
35 that film of uniform and constant thickness may be obtained at higher manufacturing take-up speeds.

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The invention also provides for films prepared from this blend having single layer construction or having laminar ABA construction wherein the A or skin layers comprise the blend of this invention and the B or core layer comprises a different olefin polymer such as high density polyethylene.

5 Films of this invention exhibit excellent elongation, tensile and impact properties and also softness, feel and noise properties which render them eminently suitable for use as back sheet components in the fabrication of absorbent articles such as diapers, bed pads and like articles where such properties are desirable.

DETAILED DESCRIPTION OF THE INVENTION

10 The very low density ethylene polymers (VLDPE) which may be used as one component in the films of this invention are ethylene/alpha-monoolefin copolymers wherein the monoolefin can have from 4-20 carbon atoms such as ethylene/butene-1, ethylene/hexene-1 and ethylene/octene-1, copolymers or terpolymers of olefins having from 4-20 carbon atoms such as ethylene/butene-1/hexene-1. These ethylene copolymers and terpolymers with prescribed range of
15 monomer levels can be prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene catalysts systems. The preferred range of comonomer level generally ranges from 4 to 15 mole percent.

20 These copolymers have a density in the range of 0.88 g/cm³ to 0.925 g/cm³. Preferably the density is in the range of 0.885 g/cm³ to 0.91 g/cm³. Densities above 0.90 g/cm³ are measured using standard accepted procedures. At densities below 0.90 g/cm³, the samples are additionally conditioned by holding them for 48 hours at ambient temperature (23°C), prior to density measurement. Preferred copolymers in accordance with the present invention are VLDPE
25 copolymers of ethylene and a C₄ to C₁₀ alpha monoolefin, most preferably copolymers and terpolymers of ethylene and butene-1 and/or hexene-1.

30 The melt index (MI) of the ethylene/alpha-mono-olefin copolymers of the present invention is in the range of 0.5 dg/min to 7.5 dg/min. Preferably the MI is in the range of 0.5 dg/min to 5.0 dg/min, and the most preferred MI is in the range of 1.0 to 2.5 dg/min. MI as measured herein is determined according to ASTM D-1238 (190/2.16). High load MI is determined according to ASTM D-1238 (190/21.6). These copolymers also have a narrow molecular weight distribution. The ratio of Mw/Mn is generally in the range of 1.5 to 3.5, preferably in the range of 2.0 to 3.0.

35 The ethylene/alpha-mono-olefin copolymers should also have an essentially single melting point characteristic with a peak melting point (T_m) as determined by

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Differential Scanning Colorimetry (DSC) in the range of 60°C to 115°C. Preferably the DSC peak T_m is in the range of 80°C to 100°C. "Essentially single melting point" as used herein means that at least 80% by weight of the material corresponds to a single T_m peak existing in the range of 60-115°C, and there is essentially absent from the polymer any substantial fraction of material which corresponds to a T_m peak found at a temperature higher than 115°C, i.e., "essentially" the bulk material content of the polymer corresponds to a "single" melting point peak in the 60-115°C range, and "essentially" no substantial fraction of the material has a peak melting point in excess of 115°C, as determined by DSC analysis.

DSC measurements are made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data i.e. the sample is heated at a programmed rate of 10°C/min to a temperature above its melting range. The sample is then cooled at a programmed rate of 10°C/min to a temperature below its crystallization range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI"). CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% (that is, 25% on each side) of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions generally represent a trivial portion of the resin of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurement.

From the weight fraction versus composition distribution curve the CDBI is

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determined by establishing what weight percent of the sample has a comonomer content within 25% each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

The resins of the present invention have CDBI's generally in the range of greater than 70 to 98%, usually in the range of 75-98% and most typically in the range of 85-95%. Obviously, higher or lower CDBI's may be obtained using other catalyst systems with changes in the operating conditions of the process employed.

A class of highly active olefin catalysts known as metallocenes may be used in the preparation of these VLDPE copolymers. These catalysts, particularly those based on Group IVB transition metals such as zirconium, titanium and hafnium, show extremely high activity in ethylene polymerization. Metallocenes are well known especially in the preparation of polyethylene and copolyethylene-alpha-olefins. For the purposes of this patent specification the term "metallocene" is herein defined to contain one or more cyclopentadienyl moiety in combination with a transition metal of the Periodic Table of Elements. The metallocene catalyst component is represented by the general formula $(Cp)_mMR_nR'_p$ wherein Cp is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IV, V or VI transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M. Various forms of the catalyst system of the metallocene type may be used in the polymerization process of this invention. Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in the disclosure of U.S. Patent No. 4,871,705 to Hoel, U.S. Patent No. 4,937,299 to Ewen, et al. and EP-A-0 129 368 published July 26, 1989, and U.S. Patent Nos. 5,017,714 and 5,120,867 to Welborn, Jr. all of which are fully incorporated herein by reference. These publications teach the structure of the metallocene catalysts and include alumoxane as the cocatalyst. There are a variety of methods for preparing alumoxane one of which is described in U.S. Patent 4,665,208. Other cocatalysts may be used with metallocenes, such as trialkylaluminum compounds; or ionizing ionic activators or compounds such as, tri (n-butyl) ammonium tetra (pentafluorophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing ionic compound. Such compounds are

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described in EP-A-0 520 732, EP-A-0 277 003 and EP-A-0 277 004 both published August 3, 1988, and U.S. Patent Nos. 5,153,157 and 5,198,401 and are all herein fully incorporated by reference. Further, the metallocene catalyst component can be a monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane or an ionic activator to form an active polymerization catalyst system to produce polymers useful in this present invention. These types of catalyst systems are described in, for example, PCT International Publications WO 92/00333 published January 9, 1992, U.S. Patent Nos. 5,096,867 and 5,055,438, EP-A-0 420 436 and WO 91/ 04257 all of which are fully incorporated herein by reference. In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbollides in combination with a transition metal. Additionally it is not beyond the scope of this invention that the catalysts and catalyst systems may be those described in U.S. Patent No. 5,064,802 and PCT publications WO 93/08221 and WO 93/08199 published April 29, 1993 all of which are herein incorporated by reference. All the catalyst systems described above may be, optionally, prepolymerized or used in conjunction with an additive or scavenging component to enhance catalytic productivity.

Utilizing a metallocene catalyst, the VLDPE copolymers useful as the low melting polymers of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

A slurry polymerization process generally uses super-atmospheric pressures and temperatures in the range of 40-100°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be an alkane, cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

Alternatively, the VLDPE copolymer component of the present invention may be formed by gas-phase polymerization. A gas-phase process utilizes super-atmospheric pressure and temperatures in the range of 50°C-120°C. Gas phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Ethylene, comonomer, hydrogen and an inert

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diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperatures of 50°C-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other impurities. Polymer product can be withdrawn continuously or semicontinuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal.

The VLDPE copolymers of the present invention can also be produced in accordance with a high pressure process by polymerization ethylene in combination with other monomers such as butene-1, hexene-1, octene-1, or 4-methylpentene-1 in the presence of the catalyst system comprising a cyclopentadienyl-transition metal compound and an alumoxane compound and the catalyst systems described above. It is important, in the high-pressure process, that the polymerization temperature be above 120°C but below the decomposition temperature of the polymer product and that the polymerization pressure be above 500 bar (kg/cm²). In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in the process of this invention.

The low to medium density ethylene polymer with which the VLDPE is blended to form the improved films of this invention may be characterized by a density in the range of from above 0.910 to 0.935 g/cm³ and generally exhibit a higher melt index than the VLDPE component, i.e., a MI above 3, preferably above 5.0 and up to 20, a molecular weight distribution above 3.5 and a compositional distribution breadth index of less than 70%, usually less than 55%. These materials may be prepared by conventional high pressure polymerization processes using free radical catalyst systems. Preferred polymers are low density polyethylene as well as low density copolymers of ethylene with up to 30 mole % of a comonomer such as propylene, vinyl acetate, acrylic acid and lower alkyl esters of acrylic acid. Preferred LDPE polymers have a preferred density in the range of from above .915 to .930 g/cm³ and a preferred MI in the range of from 5 to 15.

The blend composition of the monolayer film contains from 25 to 90% by

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weight of the VLDPE and correspondingly from 75 to 10% by weight of the low to medium density ethylene polymer, each based on the total weight of polymer present in the composition. More preferred levels range from 50 to 80% by weight of the VLDPE component, most preferably from 50 to 70% by weight of the VLDPE component.

As indicated above, the present invention also provides an embodiment wherein films of ABA construction may be prepared wherein the above described blend comprises the skin or A layers, and a different polyolefin polymer comprises the core or B layer. Because of the extremely good physical properties of films prepared from the VLDPE/LDPE blend material and particularly because of the enhanced noise reduction and softness properties of such films, such an ABA construction permits the utilization as the B core layer a material which might not otherwise be desirable for the fabrication of back sheet material due to excessive noise, poor feel or other factors. Such materials include conventional high density polyethylene having a density in the range from .940 to .980 g/cm³ and particularly scrap high density polyethylene which has been recycled and reclaimed, such as that reclaimed from milk or soft drink containers. Thus the invention provides for cost effective re-use of such materials and environmental benefits. The core layer may also contain minor amounts of the composition of the outer or skin layers so occasioned by the recycle of scrap or trim film back into the extruder to be mixed with the polymer used to prepare the core layer.

The films of the present invention may be fabricated using cast extrusion techniques well known in the art. For example, the monolayer film may be prepared by forming a uniform mixture of the polymer components and any other additives in a compounder extruder, extruding the mixture through a flat die at a temperature above the melting points of the polymer components, e.g. at temperatures from about 245°C (475°F) to about 290°C (550°F), to form a web, and casting the web on a chilled, smooth or patterned surface casting roll. For many applications it is preferred to emboss the cast film to produce a roughened pattern on the film surface such as disclosed in U.S. Patent 4,436,520 to reduce the surface gloss of the film. This embossing may be carried out using a casting roll having a patterned surface and a pressure roll wherein the web is passed through the nip of these rolls. The resulting film is then cooled and wound, or the film may be further oriented by drawing in one or two mutually perpendicular directions by techniques well known in the art.

Where the film is a laminar film of ABA construction, the film may be

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prepared by the technique described above using coextrusion techniques. Thus the polymer forming the core layer, i.e., HDPE, is coextruded with the two outer layers using a multiple die coextruder, or molten layers of the outer layers may be applied to the surfaces of an extruded cast film of the core layer.

5 A particular advantage associated with films prepared using the polymer blend components of this invention is that the film exhibits improved draw resonance properties during the production processing steps.

The films of this invention may have an overall film thickness in the range of from about 12 to about 52 μ (0.50 to 2 mil), more preferably from about 19 μ to about 40 μ (0.75 to 1.5 mil). Where ABA type laminar films are prepared, the
10 core B layer may constitute from 20 to 75% by weight of the total film, more preferably from 25 to 60% by weight of the total film.

The polymer components used to fabricate the films of the present invention may also contain effective amounts of other additives normally included
15 in such compositions. These include slip agents such as talc, antioxidants, fillers, dyes, pigments, radiation stabilizers, plasticizers and like additives.

For diaper backing applications, it is preferred to incorporate into the composition a light-colored pigment masterbatch concentrate (MB) composition which may contain a mixture of pigment, antioxidant, dispersant and other
20 additives dispersed in a suitable olefin polymer matrix.

EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered as related to actual tests performed in the practice of this invention, and illustrate the
25 benefits of this present invention and not intended as a limitation on the scope of the invention.

EXAMPLE 1

A monolayer film was prepared by mixing a polymer formulation having the composition set forth below in a 8.89 cm (3 1/2 inch) Black Clawson extruder and melt extruding a web of the polymer at a temperature of approximately 260°C
30 (500°F) vertically down into the nip between an embossing chill roll having a matte surface and a smooth surface rubber roll. The chill and rubber rolls were maintained at a temperature of 130 to 140°C and 50 to 60°C respectively and at a contact pressure of 276 kPa (40 psi) to yield film material exiting the roll nip
35 having an average thickness of 31 μ to 33 μ (1.2 to 1.3 mil). The resulting film was picked off the chill roll by a secondary chill roll maintained at 60°C, taken up

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and wound at an initial speed of 254 cm/sec (500 ft/min) to yield a finished film having a thickness in the order of 20 μ to 25 μ (0.8 to 1.0 mil).

Once the system had stabilized under the aforementioned conditions, the rate of take-up (draw line speed) was slowly increased by increasing the speed of the take-up rolls and each film observed for the appearance of draw resonance as evidenced by light and dark bands running across the film.

The composition of the monolayer film prepared above was as follows:

- a) 70% by weight of a very low density polyethylene based on a copolymer of ethylene and less than 10 mole% butene-1 having a density of 0.88 g/cm³ and a Melt Index of 2.0 dg/min.;
- b) 25% by weight of a high pressure low density polyethylene homopolymer having a density of 0.917 g/cm³ and a Melt Index of 12.0 dg/min.;
- c) 5% by weight of a masterbatch white pigment concentrate dispersed in polyethylene component (b).

CONTROL A

A control monolayer film was prepared as set forth in Example 1 with the exception that a linear low density polyethylene was substituted for VLDPE component (a) and in the same amount. This LLDPE was a copolymer of ethylene and 3.5 mole% of hexene-1 having a density of 0.918 and a Melt Index 2.0

Films made from the composition of Example 1 and Control A were drawn at an initial rate of 254 cm/sec (500 ft/min) which speed was increased gradually to over 305 cm/sec (600 ft/min). The film of Example 1 drew down to a thickness of 14 μ (0.55 mil) at a speed of 319 cm/sec (627 ft/min) prior to breaking, with no indication of draw resonance up to the point where the film tore off. The Control A film exhibited draw resonance prior to reaching a draw speed of 305 cm/sec (600 ft/min).

EXAMPLES 2 AND 3

Example 1 was repeated using two additional formulations wherein the film components used in Example 1 were present at the following levels:

- Ex. 2 - (a) VLDPE - 50% by weight
- (b) LDPE - 45% by weight
- (c) Pigment concentrate - 5% by weight
- Ex. 3 - (a) VLDPE - 30% by weight
- (b) LDPE - 65% by weight
- (c) Pigment concentrate - 5% by weight

Films were drawn at a rate of 254 cm/sec (500 ft/min). Physical properties

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of these films as well as the Control A and Example 1 film (also drawn at 254 c/sec (500 ft/min.)) are shown in Table 1.

TABLE 1

Film	Control A	EX. 1	EX. 2	EX. 3
YAG ₁ (mil)	1.20	1.23	1.25	1.25
YAG ₁ (μ)	30.48	31.24	31.75	31.75
Dart Impact (g)	166	338	262	230
TD ₂ Ult. Tens. (g/in)	1740	2672	2117	1754
TD ₂ Ult. Tens. (g/cm)	685.0	1052.0	833.5	690.6
TD Ult. Elon. (%)	671	733	698	676
TD Sec. Mod. (psi)	NT*	12,430	14,170	14,570
TD Sec. Mod. (kPa)	NT*	85705	97702	100460
MD ₃ Ult. Elong. (%)	482	574	471	416
MD Ult. Tens. (g/in)	2148	3093	2484	2133
MD Ult. Tens. (g/cm)	845.7	1218	978	840
MD Sec. Mod. (psi)	NT*	11,910	14,070	13,820
MD Sec. Mod. (kPa)	NT*	82120	97013	95289

1 YAG - Average film thickness calculated based on film weight and polymer density

2 TD - Transverse direction

3 MD - Machine direction

NT* - Not tested

EXAMPLES 4, 5 AND 6

Three additional formulations were prepared and processed into monolayer film by the method set forth in Example 1. Components were blended at the following levels:

- | | | |
|----|----------------------|-----------------|
| a) | VLDPE* | - 67% by weight |
| b) | LDPE (Same as Ex. 1) | - 28% by weight |

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c) Pigment Concentrate - 5% by weight

*In Example 4, the VLDPE used was a copolymer of ethylene and butene-1 having a melt index of 2.2 and a density of 0.885.

In Example 5, the VLDPE used was a copolymer of ethylene and hexene-1 having a melt index of 2.2 and a density of 0.889.

In Example 6, the VLDPE used was a copolymer of ethylene and hexene-1 having a melt index of 2.2 and a density of 0.906.

CONTROL B

Example 1 as repeated with the same level of ingredients as in Examples 4-6 with the exception that a linear low density polyethylene (LLDPE) was substituted for the VLDPE and in the same amount. The LLDPE used in this Control was a copolymer of ethylene and octene-1 having a Melt Index of 2.5 and a density of 0.935.

Films made from the formulation of Examples 4-6 and Control B were cast and embossed to yield an average post emboss film gauge of 30.5 μ (1.2 mils) and drawn at an initial line speed of 254 cm/sec (500 ft/min). For each film, the line speed was gradually increased until the film tore. Table 2 reports the melt temperature of the composition exiting the extruder, the observation of Draw Resonance, the film thickness just before the film tore and the film speed at the time of tear.

TABLE 2

	Melt Temperature		Draw Resonance	Film Thickness at Tear		Speed at Tear
	(°C)	(°F)		(μ)	(mil)	cm/sec ft/min
EX. 4	263	506	None	19.1	0.75	411.5 810
EX. 5	262	504	None	14.5	0.57	541.5 1066
EX. 6	265	509	None	17.8	0.70	443.8 872
Control B	267	513	Yes (Prior to 305 cm/sec (600 ft/min))	17.0	0.67	467.4 920

As shown by the data in Table 2, none of the films made using formulations within the scope of this invention exhibited draw resonance prior to film tear, whereas the formulation of Control B exhibited draw resonance prior to draw speeds of 305 cm/sec (600 ft/min).

As indicated above, this invention also provides for laminar films of ABA construction wherein the A, or skin layers, comprise the blends of this invention

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and the B, or core layer, comprises a different polyolefin such as high density polyethylene. The following example illustrates the preparation of such a laminar film.

EXAMPLE 7

5 An ABA laminar film was prepared by coextruding a ground up, reclaimed high density polyethylene having a density of $.9616 \text{ g/cm}^3$ and the composition of Example 1 containing a mixture of 70% by weight of VLDPE, 25% by weight of LDPE and 5% by weight of pigment concentrate. These materials were coextruded at 270.6 to 294.4°C (519 to 526°F) through a coextrusion die at a rate
10 of 101.4 kg/hr (400 lbs/hr) in a configuration such that the HDPE formed the core B layer and the VLDPE mixture formed the skin A layers. The resultant film had a thickness of 30.5μ (1.2 mil) with the core layer having thickness of 7.62μ (0.30 mil) and each skin layer a thickness of 11.4μ (0.45 mil)

CONTROL C

15 Example 7 was repeated except that a linear low density polyethylene (based on a copolymer of ethylene and 1-octene) was substituted for the VLDPE component of the skin layer formulation. The LLDPE had a melt index of 2.0 and a density of 0.918. The resulting film had a thickness of 30.5μ (1.2 mil), with a core layer thickness of 7.62μ (0.30 mil) and skin layer thickness of 11.4μ (0.45 mil) each.
20

Properties of the resulting films are shown in Table 3.

TABLE 3

Film	EX. 7	Control C
CD-10%	562	672
TD-Break (g/in)	2668	2247
TD-Break (g/cm)	1050.4	884.6
TD-Elong (%)	702	693
MD-Break (g/in)	3023	1926
MD-Break (g/cm)	1190.2	758.3
MD-Elong (%)	583	396
Dart Impact (g)	198	123

Note: CD-10% - Tensile strength at 10% Elongation

TD-Break - Tensile strength at break(transverse direction)

TD-Elong - Elongation at break (transverse direction)

MD - Machine direction

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As shown in Table 3, laminar films of the present invention exhibit markedly better physical and mechanical properties when compared with a comparable film containing a LLDPE instead of VLDPE in the skin layers.

CLAIMS

We Claim.

1. A polymer composition comprising a mixture of:
 - 5 a) 25 to 90% by weight, based on polymer content, of a copolymer of ethylene and a C₄ to C₂₀ alpha-monoolefin comonomer, said copolymer having a density of from 0.88 to 0.925 g/cm³, a melt index of from 0.5 to 7.5 dg/min, a molecular weight distribution of no greater than 3.5 and a compositional distribution breath index greater than 70 percent, and
 - 10 b) 10 to 75% by weight, based on polymer content, of a low to medium density ethylene polymer having a density in the range of from 0.910 to 0.935 g/cm³, a melt index of from 0.5 to 20 dg/min, a molecular weight distribution above 3.5 and a compositional breath index of less than 70%.
- 15 2. A method of reducing draw resonance during the production of polyolefin film material comprising:
 - i) forming a polymer mixture in accordance with claim 1;
 - ii) melt extruding said mixture at a temperature of up to 288°C into a nip formed by a casting roll and a pressure roll; and
 - 20 iii) taking-up said film from said casting roll at a linear speed in excess of 254 cm/sec.
3. A film prepared from the composition of claim 1 or the method of claim 2.
- 25 4. The composition of any of the preceding claims containing from 50 to 80% by weight of component (a) and from 20 to 50% by weight of component (b).
5. The composition of any of the preceding wherein component (b) is a low
30 density ethylene polymer having a density of above 0.915 g/cm³.
6. The composition of any of the preceding claims wherein said component (b) is an ethylene polymer having a melt index of from 5 to 15 dg/min.
- 35 7. The composition of any of the preceding claims wherein said ethylene copolymer (a) contains from 4 to 15 mole percent of said comonomer.

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8. The composition of any of the preceding claims wherein said component (a) is a terpolymer comprising said copolymer of ethylene and said C₄ to C₂₀ alpha-mono-olefin and an additional C₄ to C₂₀ alpha-olefin different from said alpha-mono-olefin.
9. The film of claim 2 or 3 having a thickness in the range of from 12 μ to 52 μ .
10. The film of claim 2 or 3 which is a monolayer film.
11. The film of claim 2 or 3 which is a laminar film of ABA construction wherein each A layer comprises said mixture and said B layer comprises a different polyolefin composition.
12. The film of claim 11 wherein said B layer is HDPE or recycled HDPE.
13. The film of claim 11 wherein said B layer comprises from 20 to 75% by weight of said film.
14. An article of manufacture made from the film of claim 2 or 3.
15. The process of claim 2 wherein said melt extrusion temperature is at least 246°C.
16. The process of claim 2 wherein said casting roll has an embossed surface to provide a film having a matte surface.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 93/08586

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L23/04 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 244 982 (EL PASO PRODUCTS) 11 November 1987 see page 2, line 1 - line 50 ---	1-10
Y	WO,A,90 03414 (EXXON CHEMICAL PATENTS) 5 April 1990 Abstract see page 2, line 3 - page 5, line 22 ---	1-10
A	EP,A,0 461 848 (MITSUI PETROCHEMICAL INDUSTRIES) 18 December 1991 see claim 1 -----	2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- *E* earlier document but published on or after the international filing date
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

23 December 1993

Date of mailing of the international search report

13. 01. 94

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INTERNATIONAL SEARCH REPORT
information on patent family members

Inter. Application No
PCT/US 93/08586

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0244982	11-11-87	US-A-	5051297	24-09-91
		US-A-	5066724	19-11-91
WO-A-9003414	05-04-90	AU-B-	615804	10-10-91
		AU-A-	4338089	18-04-90
		EP-A-	0389611	03-10-90
		JP-T-	3502710	20-06-91
EP-A-0461848	18-12-91	JP-A-	4103649	06-04-92
		JP-A-	4120144	21-04-92
		CN-A-	1057276	25-12-91
		JP-A-	4226141	14-08-92
		US-A-	5262228	16-11-93

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